



Dietary exposure to perfluoroalkyl acids of specific French adult sub-populations: High seafood consumers, high freshwater fish consumers and pregnant women

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HIGHLIGHTS

- The dietary exposure was estimated for 15 perfluoroalkyl acids.
- Despite the overestimation, the FFQ remains useful to evaluate the whole diet.
- The high fish consumers are the most dietary exposed population.
- Fishery products are the main exposure contributors under LB hypothesis.

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ABSTRACT

Perfluoroalkyl acids (PFAAs) are globally found in various media, including food and especially fishery products. In the present study, the dietary exposure to 15 perfluoroalkyl acids was assessed for 3 French adult populations, namely high seafood consumers, high freshwater fish consumers, and pregnant women. Purified food extracts were analysed by LC–MS/MS and PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFTrDA, PFTeDA, PFBS, PFHxS, PFHpS, PFOS and PFDS were monitored and quantified according to the isotope dilution principle. Under lower bound (LB) hypothesis (i.e. contamination values < LOD considered as 0), high freshwater fish consumers appear as the most exposed to PFOS (7.5 ng.kg⁻¹ bw.d⁻¹), PFUnA (1.3 ng.kg⁻¹ bw.d⁻¹), PFDA (0.4 ng.kg⁻¹ bw.d⁻¹) and PFHpS (0.03 ng.kg⁻¹ bw.d⁻¹) while high seafood consumers appear as the most exposed to PFOA (1.2 ng.kg⁻¹ bw.d⁻¹), PFNA (0.2 ng.kg⁻¹ bw.d⁻¹) and PFHxS (0.06 ng.kg⁻¹ bw.d⁻¹). For all considered populations, the major exposure contributors are fish, seafood and water under LB hypothesis, while dairy products, bread and crispbread are the main contributors under upper bound (UB) hypothesis. Besides this food exposure assessment, further studies are needed to assess the more global PFAA exposure, taking into account indoor and outdoor air, dust and cutaneous contact, which could be other important contributors for this particular class of chemicals.

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1. Introduction

Perfluoroalkyl acids (PFAAs) refer to a group of anthropogenic chemicals with a fully fluorinated alkyl chain, first put on the market

in 1956 as a textile-protectors. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are main representatives of two major sub-classes of PFAAs, namely perfluoroalkyl sulfonic acids and perfluoroalkyl carboxylic acids, respectively. Their chemical structure confers to these amphiphilic substances a high thermal and chemical stability as well as surface tension lowering properties (Key et al., 1997). These characteristics are used for an extended range of products such as fire-fighting foams, cleaning-agents, food-contact papers, inks, varnishes, lubricants, metal plating, stain and soil repellents for leather, textiles and paper. However, this stability led to an environmental contamination including water, sediment, air, aquatic and terrestrial biota at ng.g⁻¹ levels, along with a high persistence in the environment (Giesy and Kannan, 2001; Prevedouros et al., 2006), also due to the

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limited effectiveness of current water treatments to remove these compounds released by PFAA manufacturing plants or consumer products (Dauchy et al., 2012). As a consequence, the use or the consumption of contaminated water is one of the PFAA entry points in the food chain. Serum half-life in human has been estimated to be 5.4, 3.8 and 8.5 years for PFOS, PFOA and perfluorohexane sulfonate (PFHxS) (Olsen et al., 2007). Epidemiological studies suggest a positive association between PFOS serum level and infertility (La Rocca et al., 2012), PFOA serum level and osteoarthritis (Innes et al., 2011) or obesogenic effects (Halldorsson et al., 2012), PFOS and PFOA cord serum level and allergic status (Wang et al., 2011) as well as thyroid disease (Melzer et al., 2010) and chronic kidney disease (Shankar et al., 2011). However, these associations are still under debate, and the contribution of these substances with regard to these pathologies remains difficult to establish with an unambiguous level of proof.

Among the multiple pathways characterising the human exposure to PFAA, food intake is thought to be the major contemporary one for the general adult population (Vestergren and Cousins, 2009), representing about 90% of the total exposure. Moreover, fishes appear to be major contributors to PFAA food exposure regarding their contamination levels more elevated than other foodstuffs, and the also high consumed quantities (Tittlemier et al., 2007). The European Food Safety Authority gathered food contamination data from 13 European countries to assess the general population dietary exposure for 27 per- and polyfluoroalkylated substances, including PFAAs. The exposure levels were estimated to be in mean and high percentiles respectively in the range of <0.01 ng per kg of body weight per day ($\text{ng}\cdot\text{kg}^{-1}\cdot\text{bw}\cdot\text{d}^{-1}$) to $5.2\text{ ng}\cdot\text{kg}^{-1}\cdot\text{bw}\cdot\text{d}^{-1}$ and in the range of $<0.01\text{ ng}\cdot\text{kg}^{-1}\cdot\text{bw}\cdot\text{d}^{-1}$ to $10\text{ ng}\cdot\text{kg}^{-1}\cdot\text{bw}\cdot\text{d}^{-1}$, depending on the compound (EFSA, 2012).

The aim of the present study was to assess the dietary exposure to 15 PFAAs for three particular sub-population at French level, namely high seafood and freshwater fish consumers, as part of the most dietary exposed populations, as well as mother–newborn pairs, as highly vulnerable population with regard to the chemical risk. The estimated exposure levels were then compared between these particular populations for which new data were presently generated and other populations, namely French general population and another mother–infant population for which data were already available.

2. Subjects and methods

2.1. Populations and food consumption data

Three food consumption datasets were studied: the 2006 CALIPSO study on French high marine fish and seafood consumers, the 2011 ICAR-PCB study on French anglers and members of their family and the 2010–2013 CONTREPERF ANR programme, a study which included French pregnant women. The dietary consumption assessing methodology for CALIPSO and ICAR-PCB studies has already been described elsewhere (Desvignes et al., 2012; Sirot et al., 2008). Briefly, the CALIPSO study included 993 adult high seafood consumers (seafood consumption frequency \geq twice a week) in 4 French coastal areas: Gironde-South Charente Maritime, Normandy-Baie de Seine, South Brittany and Mediterranean-Var. The ICAR-PCB study included 606 adults, anglers and members of their family, representing 21,180 angler households in 6 areas corresponding to the 6 major French rivers. The CONTREPERF programme included 106 pregnant women from 20 to 46 years between 2010 and 2013 in the Toulouse university hospital with a planned caesarean section. The CALIPSO, ICAR-PCB and CONTREPERF subjects completed a food frequency questionnaire (FFQ), with a mention of before and during pregnancy for the pregnant women. For each study, the portion sizes were estimated using sample photographs of a validated manual (Hercberg et al., 1994). Four groups were defined for the anglers and members of their household, according to their freshwater fish consumption frequency. The upper

quartile ($n = 142$, frequency ≥ 45 times per year) was considered as the high freshwater fish consumers (Q4).

2.2. Contamination data

Food sampling methodology and contamination data have already been described elsewhere for the seafood and marine fishes, freshwater fishes and the food items from the total diet study (Desvignes et al., 2012; Rivière et al., submitted for publication; Sirot et al., 2008, 2009; Yamada et al., submitted for publication).

Briefly, sampling for the general population total diet has been conducted between 2007 and 2009 for the second French total diet study (TDS), based on the INCA2's consumption data analysis (individual and national study on food consumption 2). Each of the 599 samples constituted by 15 primary samples was prepared "as consumed" (peeled, boiled, raw...) and took into account geographical, seasonal variations and consumption habits to cover 90% of the consumption rate. A sampling list of the most consumed seafood according to the analysis of the CALIPSO study's FFQ was established by coastal area, taken into account regional consumption and contamination differences for the 5 primary samples constituting the composite sample. Sampling in each area was conducted in 2005 for a total of 159 composite samples for 29 fish species, 16 mollusc and crustacean species and 21 canned products, smoked fishes or seafood-based products. This sampling covered 88 to 100% of the seafood consumption rate of high seafood consumers, depending on the considered area. Only the raw edible part was analysed for fresh and frozen products. A sampling list of the most consumed freshwater fishes was established according to the analysis of the ICAR-PCB study's FFQ. The 387 composite samples are issued from the 2008–2009 ONEMA (French National Agency for Water and Aquatic Environments) freshwater fish library and concerned 16 species from the 6 major French rivers and their tributaries. This sampling covered almost 100% of the freshwater fish consumption rate of the anglers and members of their family.

The used methodology targeted 15 PFAAs: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluoroheptane sulfonate (PFHpS), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorotridecanoic acid (PFTeDA), perfluorotetradecanoic acid (PFTeDA), perfluorobutane sulfonate (PFBS), PFHxS, PFOS and perfluorodecane sulfonate (PFDS). Analytical procedure used for PFAA determination was described elsewhere (Kadar et al., 2011). Briefly, samples were pre-treated by freeze-drying and liquid/solid extraction with methanol. A dispersive SPE based on charcoal particles was then applied. Final purified extracts were analysed by liquid chromatography coupled to tandem mass spectrometry (LC–MS/MS) with negative electrospray ionisation on a triple quadrupole system. Two diagnostic signals (MRM transitions) were recorded for each targeted analyte. Quantification was performed according to the isotope dilution principles: each sample was supplemented by 11 ^{13}C -labelled internal standards ($^{13}\text{C}_4$ -PFOA, $^{13}\text{C}_4$ -PFOS, $^{13}\text{C}_4$ -PFBA, $^{13}\text{C}_5$ -PFHxA, $^{13}\text{C}_4$ -PFHpA, $^{13}\text{C}_5$ -PFNA, $^{13}\text{C}_2$ -PFDA, $^{13}\text{C}_7$ -PFUnA, $^{13}\text{C}_2$ -PFDoA, $^{18}\text{O}_2$ -PFHxS, and $^{13}\text{C}_4$ -PFOSi). Limits of detection (LOD), depending on the considered fish species and target compound were determined based on the signal-to-noise ratio ($S/N > 3$) and ranged from 0.005 to $0.3\text{ ng}\cdot\text{g}^{-1}$ for PFOA and PFOS, and from 0.007 to $0.95\text{ ng}\cdot\text{g}^{-1}$ for other PFAA substances. Repeatability of the signal was also dependent of the matrix, but was globally estimated below 18.6% for all compounds.

LABERCA operates under ISO/IEC 17025:2005-certified Quality Assurance system implicating several procedures related to the specification and validation of personnel, methods and instrumental conditions. The laboratory is also certified based on the ISO 9001:2008 standard for all its research activities including methodological development. In addition, the laboratory is regularly taking part in interlaboratory comparison tests and has proven satisfactory results for this method.

Blank and quality control samples were analysed and monitored in parallel with the samples to be characterised: the signal of each compound in the blanks was checked to ensure the absence of contamination throughout the analytical procedure, and concentrations of analytes in quality control were monitored to check the method repeatability.

2.3. Dietary exposure assessment

Individual dietary exposure was estimated by combining individual food consumption data, food contamination and individual body weight, according to the formula below:

$$E_{i,j} = \frac{\sum_{k=1}^n C_{i,k} L_{k,j}}{BW_i}$$

where $E_{i,j}$ is the daily exposure of the subject i to the PFAA j ($\text{ng.kg}^{-1} \text{bw.d}^{-1}$), $C_{i,k}$ is the daily intake of the food item k by the subject i (g.d^{-1}), $L_{k,j}$ is the mean concentration of the PFAA j in the food item k (ng.g^{-1} wet weight), n is the number of foods in the diet of the subject i , and BW_i is the body weight of the subject i (kg). Table 1 summarizes the datasets used for the dietary exposure assessment. The contamination data for the whole diet and the dietary exposure of the French general population are issued from the French second total diet study (Rivière et al., submitted for publication).

As far as the consumption frequencies fulfilled by the CONTREPERF pregnant women included not individual but grouped food items, and considering the expected wide range of contamination levels in various fish and seafood products, the selection of fish species for reconstituting that food contamination was based on the adult woman consumption in the INCA2 study which is representative of the French general population (Dubuisson et al., 2010). For freshwater fishes, brown trout (*Salmo trutta fario*), European perch (*Perca fluviatilis*), zander (*Sander lucioperca*), common carp (*Cyprinus carpio carpio*), northern pike (*Esox lucius*) and European eel (*Anguilla anguilla*) were the only species consumed by the French female general population and all of them were selected. For marine fishes and seafood, most consumed species were again considered (consumption rate > 5% of the total marine fish or seafood consumption), namely canned tuna, salmon (*Salmo salar*), breaded fish (TDS2 sampling), smoked salmon, saithe/coalfish (*Pollachius virens*), Atlantic cod (*Gadus morhua*), canned sardine (*Sardina pilchardus*), shrimp, mussel, great scallop (*Pecten maximus*), oyster and squid (*Loligo vulgaris*). The mean contamination determined for seafood, marine and freshwater fishes was weighted according to the selected species consumption rates.

As the measured contamination levels were found below the limit of detection for higher than 60% of the analysed food samples, with LOD equally low in the three studies, the 1995 WHO GEMS/Food-EURO workshop recommendations were applied (World Health Organization-Global Environment Monitoring System-Food Contamination Monitoring and Assessment Programme) (GEMS/Food-EURO, 1995). Two exposure scenarios were then defined, the lower bound scenario (LB), where any data below the LOD was replaced by a null contamination, and the upper bound scenario (UB), where any data below the LOD

was replaced by the LOD value. This approach allows surrounding the real dietary exposure value. The two exposition scenarios are presented, taking into account uncertainty arising from analyses.

2.4. Data and statistical analysis

Normality of the distributions was tested with Kolmogorov–Smirnov test and homoscedasticity with Bartlett test. Wilcoxon–Mann–Whitney test was used to compare the mean exposure between 2 groups, Kruskal–Wallis test if more than 2 groups. Ward's method has been applied for the hierarchical cluster analysis to define 3 groups of freshwater fishes (low, medium and high levels of PFAA contamination, for fishes with $n \geq 5$). Differences between groups are considered as significant if $p < 0.05$. All statistical analyses were performed using SAS software 9.3 (SAS Institute Inc., Cary, NC, USA).

3. Results and discussion

Table 2 briefly presents the food contamination distribution for the sum of the 15 PFAAs from the three studies. Fishes, and especially the freshwater ones, appear clearly to be the most contaminated food group. The hierarchical cluster analysis applied to these contamination data revealed the existence of 3 distinct groups of freshwater fishes. The low contamination level group includes brown trout *S. trutta fario*, freshwater bream *Abramis brama*, northern pike *E. lucius*, thicklip grey mullet *Chelon labrosus* and wels catfish *Silurus glanis*. The medium one includes bleak *Alburnus alburnus*, chub *Squalius cephalus*, common carp *C. carpio carpio*, European eel *A. anguilla*, European perch *P. fluviatilis*, silver bream *Blicca bjoerkna* and zander *S. lucioperca*. The high one includes barbel *Barbus barbus* and gudgeon *Gobio gobio*. However, for some species for which only a low number of samples were considered, like gudgeon or barbel ($n = 5$), the link between the measured contamination level and the bioaccumulation potency or other factors such as the geographical localisation or the specimen's age remains difficult to establish. As far as all the freshwater fishes were wild fishes sampled from different areas of the 6 major French rivers or their tributaries, it can be assumed that these wild fishes were exposed to the PFAAs released by human activities like the use of consumer products (fried pan with anti-sticking coating, carpet treatment...) or the PFAS manufacturing plant discharge as shown in a French study. Differences between freshwater and marine fish contamination levels could be due to the greater PFAA dilution in seas and/or due to some difference of lifestyle (for example distance from sediment, diet...), but has to be confirmed by further studies.

In Table 3 the assessed dietary exposure per compound and per population for PFOA, PFNA, PFDA, PFUnA, PFHxS, PFOS and PFHpS is presented and compared to the dietary exposure of the French adult general population from the French TDS2 study (Rivière et al., submitted for publication) and to another French pregnant woman population from the EDEN study (Chan-Hon-Tong et al., 2013). These 7 compounds correspond to those for which a detection rate equal or higher than 25% was observed in the maternal and cord serum of the CONTREPERF mother–infant population (Cariou et al., 2013). The details

Table 1
Summary of used datasets and percentage data below the LOD.

Population	n	Consumption data	Food contamination data (% data < LOD)
High seafood consumers	993	CALIPSO study	<ul style="list-style-type: none"> Marine fish and seafood: CALIPSO sampling (69.9%) Other food items: French TDS2* (99.3%)
Anglers and household	606	ICAR-PCB	<ul style="list-style-type: none"> Freshwater fish: ICAR-PCB sampling (64.3%) Marine fish and seafood: CALIPSO sampling (69.9%) Other food items: French TDS2 (99.3%)
Pregnant women	106	CONTREPERF programme	<ul style="list-style-type: none"> Marine fish and seafood: CALIPSO sampling (69.9%) Freshwater fish: ICAR-PCB sampling (64.3%) Other food items: French TDS2 (99.3%)

Table 2

Food contamination distribution from TDS2, CALIPSO and ICAR-PCB studies, sum of the 15 PFAAs (ng.g^{-1}) on food groups (TDS2) or on species (CALIPSO and ICAR-PCB). Standard deviation = Std, Minimum value = Min, Maximum value = Max.

Study	Food items	LB			UB		
		Mean	Std	Min–Max	Mean	Std	Min–Max
TDS 2	Whole diet ^a	0.0	0.0	0–0.2	1.7	0.9	0.1–3.6
CALIPSO	Marine fish	2.9	1.6	0.3–6.8	3.3	1.5	1.1–7.1
	Mollusk, crustacean, shellfish	1.7	2.1	0.0–7.0	2.2	2.1	0.2–7.5
	Canned, smoked, seafood-based product	0.3	0.5	0–1.9	1.1	0.6	0.3–2.2
ICAR-PCB	Freshwater fish: low contamination group	16	6.2	9.4–24.5	17	6.1	10.3–25.5
	Freshwater fish: medium contamination group	47.8	20.1	30.4–88.8	49.1	20.1	32–89.5
	Freshwater fish: high contamination group	148.9	27.6	129.3–168.4	150.6	27.3	131.3–169.9

^a Fish and seafood products were excluded.

of the dietary exposure per food group for the 15 analysed PFAAs are available in the supplementary data.

Dietary exposures were significantly higher for the high seafood consumers, the high freshwater fish consumers and the pregnant women from the CONTREPERF programme compared to those for the general population ($p < 0.0001$ for the 15 PFAAs, under LB and UB hypotheses).

The women from the CONTREPERF programme are significantly less exposed by food than the women from the EDEN cohort ($p < 0.0001$ for the 15 PFAAs, under LB and UB hypotheses, except for PFTTrDA under the LB hypothesis, $p = 0.008$). These two French pregnant women populations were constituted in Poitiers and Nancy with 2002 patients recruited between 2003 and 2006 to investigate about pre- and postnatal factors of child psychomotor development health for the EDEN cohort while the CONTREPERF programme included 106 patients from Toulouse recruited from 2010 to 2013 to investigate about the PFAA transfer between the mother and the child. Surprisingly, the women from the CONTREPERF programme reported a mean freshwater fish consumption of 7.4 g per day (2.7 kg per year) before pregnancy and 11 g per day during pregnancy, whereas the adult women from the INCA2 study, representative of the French general population, reported an average consumption of 0.96 g per day of freshwater fishes. EDEN cohort women were asked for their fresh fish consumption without mention of marine or freshwater origin, so the more frequently consumed species in the INCA2 study were selected for the dietary exposure assessment, which turned out to be marine species. Individuals recruited for the INCA2 study completed a 7-day dietary record, which is known to be more accurate than a FFQ, especially in the CONTREPERF FFQ in which the consumption of the food items “marine fish” and “freshwater fish” was asked separately. Indeed, the consumption overestimation tends to increase with the number of food groups in the questionnaire. However, the CONTREPERF programme was not designed to be a robust epidemiological study but an explorative study on the environmental and dietary factors which are likely to have an effect on the serum PFAA level. Although the FFQs are less accurate than a dietary record and tend to overestimate the food consumption, especially for the food items that are rarely eaten (Vereecken et al., 2008), it remains a good cost/time compromise to assess food consumption frequencies for the whole diet. Moreover, the CONTREPERF programme questionnaire might be more subject to memory bias, as far as the women were asked to fill in the questionnaire during their delivery maternity ward stay for their habits for both before and during pregnancy periods, compared to the EDEN cohort women who filled in their questionnaire at 15 weeks of amenorrhea in average and then during the first few days following the delivery. Although a dietary record filled in during the first weeks of amenorrhea and then during the last trimester of the pregnancy would have generated more reliable data, it would have been much more difficult to recruit the expected number of individuals for the CONTREPERF programme. Taken altogether, these uncertainties could explain a large part of the observed high dietary exposure of the CONTREPERF women.

Under the LB hypothesis, the upper quartile of the anglers and household population, i.e. the high freshwater fish consumers, is the

most dietary exposed to PFDA ($0.4 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$), PFOS ($7.5 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$), PFUnA ($1.3 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$) and PFHpS ($0.03 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$). The high seafood consumers are the most dietary exposed to PFHxS ($0.06 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$), PFNA ($0.2 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$) and PFOA ($1.6 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$). Differences between the high seafood and the high freshwater fish consumers are statistically significant with a p -value below 0.0001, except for PFDA and PFDS ($p = 0.0002$ and $p = 0.0086$) under the UB hypothesis and for PFHxS and PFUnA under the LB hypothesis ($p = 0.0032$ and $p = 0.0002$). Dietary exposures were not statistically different for PFBA, PFBS, PFHxS, PFUnA and PFTeDA under the LB hypothesis. All the dietary exposure was null under the LB hypothesis for the French general population, considering the high censored data rate. Results under the UB hypothesis are difficult to assess. Indeed, dairy products appear to be the major exposure contributors even though PFAAs were detected in none of these products. Their elevated LOD and their important consumption are enough to attribute them an important weight in the total dietary exposure, especially in pregnant women who increase their dairy product consumption. The major contribution due to a high consumption is also reported for milk and dairy products in Nordic countries, accounting for respectively 25% of the PFOS dietary exposure and 24% of the PFOA dietary exposure (Noorlander et al., 2011; Vestergren et al., 2012). As supposed before, fishery product is the main contributor of the total dietary exposure to PFAAs when considering data with detected compounds, i.e. LB hypothesis. This explains the higher exposure of the high seafood and high freshwater fish consumers compared to the general population and pregnant women one. Dietary exposure for PFTeDA and PFTTrDA is underestimated, due to the lack of contamination data for numbers of food groups (bread and crispbread, breakfast cereals, sweetened pastries and biscuits, cheese, butter, offal, potatoes and related products, dried pulses, chocolate, water, sandwiches and hamburgers, condiments and sauces). Except for water, none of these products is likely to be a major exposure contributor. We assume that their contribution is negligible in the total dietary exposure for PFTeDA and PFTTrDA.

Globally, the present exposure data appear consistent with the published literature. The PFOS average dietary exposure ranges from $0.27 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$ (LB) to $5.2 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$ (UB) in the 2012 EFSA report (EFSA, 2012), $0.86 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$ to $1.4 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$ for the Swedish general population under LB hypothesis between 1999 and 2010 (Vestergren et al., 2012) and around $2.7 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$ for the Swedish high fish consumers under LB hypothesis (Berger et al., 2009). The PFOA, PFNA, PFDA, PFUnA, PFHxS and PFHpS dietary exposure ranges (mean- p_{95} under the LB hypothesis) in the 2012 EFSA report are respectively $0.08\text{--}0.22 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$, $0.03\text{--}0.06 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$, $0.02\text{--}0.04 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$, $0.03\text{--}0.05 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$, $0.05\text{--}0.11 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$ and $<0.01\text{--}<0.01 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$, but only concern the general population.

The assessed dietary exposure comparison between the different sub-population is facing some difficulties, as far as individual food consumption data were collected by different questionnaires with different – but similar – food groups. For the general population, a 7-day dietary record was used instead of a FFQ like in CALIPSO, ICAR-PCB,

Table 3
Arithmetic mean and 95th percentile of the dietary exposure of adult general population, high seafood consumers, anglers or family and their upper quartile, EDEN and CONTREPERF women before and during pregnancy ($\text{ng.kg}^{-1} \text{bw.d}^{-1}$).

Population	n	PFOA			PFNA			PFDA			PFUnA			PFHxS			PFHpS			PFOS									
		Mean			P95 ^a			Mean			P95 ^a			Mean			P95 ^a			Mean			P95 ^a						
		LB	UB	LB	LB	UB	LB	UB	LB	UB	LB	UB	LB	UB	LB	UB	LB	UB	LB	UB	LB	UB	LB	UB					
High seafood consumers	993	1.16	2.06	3.83	5.86	0.18	1	0.53	2.4	0.16	0.73	0.51	1.82	0.43	5.27	1.54	12.6	0.06	0.67	0.27	1.72	0.00	0.85	0.00	2.07	1.53	2.45	4.42	6.5
Anglers or family	606	0.15	1.23	0.48	3.24	0.03	0.86	0.09	2.41	0.08	0.64	0.34	1.91	0.19	5.06	0.75	14.49	0.02	0.66	0.04	1.8	0.00	1.06	0.02	2.73	1.17	2.13	5.24	7.84
Anglers or family Q4	142	0.23	1.27	0.76	3.32	0.07	0.86	0.21	2.36	0.42	0.96	1.54	3.02	1.28	5.8	5.96	18.29	0.05	0.69	0.13	1.82	0.03	1.06	0.14	2.61	7.51	8.42	29.74	32.08
CONTREPERF women before pregnancy	106	0.11	1.67	0.17	2.61	0.02	1.2	0.04	1.84	0.12	0.92	0.22	1.3	0.12	7.11	0.22	10.76	0.01	0.95	0.02	1.43	0.01	1.39	0.02	2.08	2.62	3.94	5.37	6.82
CONTREPERF women during pregnancy	106	0.1	1.52	0.19	2.41	0.02	1.12	0.03	1.8	0.17	0.91	0.19	1.25	0.17	6.58	0.22	10.4	0.02	0.87	0.02	1.33	0.01	1.26	0.02	1.94	4.05	5.25	4.88	6.37
Adult general population ^b	1918	0.00	0.74	0.00	1.5	0.00	0.49	0.00	0.97	0.00	0.34	0.00	0.64	0.00	3.23	0.00	6.19	0.00	0.38	0.00	0.7	0.00	0.7	0.00	1.45	0.00	0.66	0.00	1.15
EDEN women before pregnancy ^c	1861	0.01	0.83	0.01	1.60	0.00	0.71	0.01	1.40	0.01	0.49	0.03	0.99	0.02	4.12	0.09	8.40	0.01	0.52	0.01	1.03	0.00	0.79	0.00	1.55	0.03	0.78	0.09	1.51
EDEN women during 3rd trimester ^c	1775	0.01	0.82	0.01	1.53	0.00	0.71	0.01	1.38	0.01	0.49	0.03	0.96	0.02	4.20	0.08	8.41	0.00	0.51	0.01	0.98	0.00	0.78	0.00	1.44	0.03	0.77	0.08	1.42

^a 90th percentile instead of 95th percentile for CONTREPERF women.

^b Results presented in Anses (2011) and Rivière et al. (submitted for publication).

^c Results presented for PFOS and PFOA in Chan-Hon-Tong et al. (2013).

EDEN and CONTREPERF studies. Even for the studies which used a FFQ, the included subjects were not questioned about the exactly same food groups. Reconciliation between the study's food groups has been operated, which can lead to a loss of contamination accuracy when groups are merged or split.

4. Conclusion

Dietary exposure to PFAAs was assessed for 3 French adult populations: high seafood consumers, anglers or member of their household and pregnant woman. Food sample analyses showed that freshwater fish was the most contaminated food group with a level up to $168.4 \text{ ng.g}^{-1} \text{ ww}$ for the LB hypothesis when the 15 analysed PFAAs are summed, namely PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFTrDA, PFTeDA, PFBS, PFHxS, PFHpS, PFOS and PFDS. It is followed by the marine fish with a contamination level up to $6.8 \text{ ng.g}^{-1} \text{ ww}$ and seafood with $7 \text{ ng.g}^{-1} \text{ ww}$. PFAAs were hardly quantified in other food items, with a detection rate below 1%.

As a result and with regard to PFOA, PFNA, PFDA, PFUnA, PFHxS, PFHpS and PFOS (most commonly detected PFAA especially in more than 25% of cord and maternal serum indicating a significant internal exposure), high seafood consumers and high freshwater fish consumers are the most exposed population under the LB hypothesis, with fish as main dietary exposure contributor. High freshwater fish consumers are the most exposed to PFDA, PFUnA, PFHpS and PFOS at respective levels of $0.42 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$, $1.28 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$, $0.03 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$ and $7.51 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$. High seafood consumers are the most exposed to PFOA, PFNA and PFHxS at respective levels of $1.16 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$, $0.18 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$ and $0.06 \text{ ng.kg}^{-1} \text{ bw.d}^{-1}$. Under the UB hypothesis, dairy products, bread and crispbread appear to be the major dietary exposure contributor, even if PFAAs were detected in none of these samples. The three studied population showed a significantly higher exposure to the 15 PFAAs compared to the general population.

Unlike the typical persistent organic pollutants such as polychlorinated biphenyls (PCBs) and dioxins which are preferentially accumulated in fatty food of animal origin and associated to a quite well characterised exposure pattern, PFAAs are subject to more diverse exposure routes and subsequent exposure patterns. Then, besides the presently considered food exposure, further studies should attempt to assess the global exposure to PFAAs, including other media including indoor and outdoor air, dust and skin contact, the ingestion of house dust being possibly responsible of 27 to 49% of the exposure for PFHxA, PFHpA, PFNA, PFDoA and PFTeDA when diet and house dust are taken into account altogether in Sweden (Vestergren et al., 2012). This global assessment is particularly needed for young children, who spend more time on the floor and multiply hand-to-mouth contacts.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.01.089>.

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